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Final Report on:

**CONTAINERLESS LOW GRAVITY PROCESSING
OF GLASS FORMING AND IMMISCIBLE ALLOYS**

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NASA - George C. Marshall Space Flight Center
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Grant NAG8-072

September, 1990

(NASA-CR-186999) CONTAINERLESS LOW GRAVITY
PROCESSING OF GLASS FORMING AND IMMISCIBLE
ALLOYS Final Report (Alabama Univ.) 22 p

CSCI 22A

N90-28747

Unclass

63/29 0304624

CONTAINERLESS LOW GRAVITY PROCESSING OF IMMISCIBLE GOLD-RHODIUM ALLOYS

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ABSTRACT

Under normal one-g conditions immiscible alloys segregate extensively during solidification due to sedimentation of the more dense of the immiscible liquid phases. In this investigation, immiscible (hypermonotectic) gold-rhodium alloys were processed in the Marshall Space Flight Center 105 meter drop tube under low gravity, containerless conditions to determine the feasibility of producing dispersed structures. Three alloy compositions were utilized. Alloys containing 10% by volume of the gold-rich hypermonotectic phase exhibited a tendency for the gold rich liquid to wet the outer surface of the samples. This wetting tendency led to extensive segregation in several cases. Alloys containing 80% and 90% by volume of the gold-rich phase possessed completely different microstructures from the 10% samples when processed under low-g, containerless conditions. Several samples exhibited microstructures consisting of well dispersed 2 to 3 μm diameter rhodium-rich spheres in a gold-rich matrix.

1. INTRODUCTION

Over 100 binary systems are known to exhibit immiscible liquid regions (Ref. 1). An example is shown in Figure 1 for the gold-rhodium system (Ref. 2). There are many possibilities for new, better materials if techniques can be developed to process immiscible alloys to obtain fine dispersions of one phase in the other. Conceivable applications include electrical contact materials, catalytic materials, fine particle magnets and superconductors (Ref. 1).

There has been considerable interest in immiscible alloys over the past two decades because of the availability of low gravity processing. In these alloys, drastic differences in structure are expected between low-g processed samples and samples processed under normal one-g conditions (Refs. 1,3-6). When solidified under one-g conditions, separated structures are obtained in immiscible alloys due to sedimentation of the more dense of the two liquid phases. Since these highly separated structures are of little practical use, there has not been a great deal of commercial interest in most immiscible alloy systems. However, if these alloys are processed under low gravity conditions, the driving force for sedimentation is removed. Under these conditions it may be possible to form a dispersion of the two liquids during cooling and maintain this dispersed structure during solidification, assuming that separation of the two liquid phases does not occur by another gravity independent phenomena.

For fine particle dispersions formed under low-gravity conditions, Stokes' flow is thought to be of little significance. However, many

believe that the movement of droplets in the liquids due to surface tension gradients will be of more importance in low-gravity situations (Ref. 4). Obviously, diffusional growth is still present in microgravity situations. As a result, if fine dispersions are to be obtained, long solidification times should be avoided in order to control Ostwald ripening (Ref. 6).

There are several critical factors in preventing segregation during microgravity processing. Among these; (1) homogenization of the alloy in a single liquid phase region must occur, (2) solidification times must be carefully controlled, and (3) wetting tendencies for the immiscible liquid phases with the containers used must be controlled in order to prevent preferential wetting of the container surface by the minority phase constituents.

In reference to point (3), work has been carried out by several other investigators on processing immiscible alloys under low gravity conditions in attempts to produce dispersed microstructures (Refs. 4-6). However, the majority of these investigations resulted in complete separation of the immiscible phases. This separation was conjectured to be primarily due to fluid flow that resulted when the minority liquid phase perfectly wet the walls of the container. It has been postulated that when a droplet of the minority liquid touches and perfectly wets the container wall as shown in Figure 2, fluid flow is induced that may pull additional minority liquid to the wall where it too wets the wall, eventually forming a film (Refs. 7, 8). This process results in a separated microstructure composed of the minority liquid phase at the outer surface surrounding the majority liquid phase in the central region.

It should be possible to avoid this difficulty if a crucible material is selected that is preferentially wet by the majority phase as opposed to the minority liquid phase. This was demonstrated by Potard when he changed the crucible material in his experiments from Al₂O₃ to SiC for tests done in orbit. In his work, Potard obtained a fairly well dispersed microstructure in Al-In alloys when they were processed in SiC crucibles (Ref. 7).

In the experiments discussed in this paper, crucible interactions were avoided since samples were processed in a drop tube using both low-g and containerless conditions. However, there was still the possibility of the preference of one of the liquid phases for the outer surface of the sample. If this liquid was the minority phase, separation could still be the end result. If segregation occurs under low-g containerless conditions it should be possible to avoid the separation process by changing the alloy composition such that the phase with a preference for the outer surface is the majority phase.

The purpose of the current effort was to attempt to eliminate the separation driving forces resulting from both gravity and the crucible interactions with the liquid phases. Elimination of separation due to both of these effects may result in a retention of a fine dispersion in the sample before and during solidification. A drop tube offers both a low-g and containerless environment and was therefore employed

as the processing technique in this study. The work focused on the effect of low-g containerless processing on the solidification structure of immiscible alloys, with particular emphasis on the type of dispersion obtained.

2. EXPERIMENTAL PROCEDURE

A convenient way to carry out experimentation requiring relatively short duration, low gravity, containerless conditions is by using a drop tube. One such facility is the 105 meter drop tube located at the Marshall Space Flight Center (MSFC) in Huntsville, Alabama, USA. This facility permits containerless melting followed by containerless solidification during 4.6 seconds of free fall.

The drop tube consists of a 10 inch diameter stainless steel tube, 105 meters in length, which is held in a vertical orientation in the Dynamic Test Facility Building at the MSFC. Turbomolecular vacuum pumps are positioned along the tube permitting evacuation to the 10⁻⁶ Torr range. A schematic of the drop tube is shown in Figure 3 (From reference 9).

The gold-rhodium alloy system was utilized for this study. The phase diagram for this system was shown in Figure 1. This system was selected because of its relatively high monotectic temperature, which is desirable if sufficiently high cooling rates are to be obtained for solidification during the 4.6 seconds of free fall available in the MSFC drop tube. Added benefits come from the natural oxidation resistance of the alloy and the color difference between the phases, which facilitates phase differentiation in an optical microscope.

Three alloy compositions were investigated. See Table 1. The first was slightly hypermonotectic with the composition being selected to produce 10% by volume of the gold-rich immiscible liquid phase at the monotectic temperature. This alloy contained 65 atomic percent rhodium. Since there was interest in studying separation due to wetting tendencies of the minority and majority liquids, another alloy was produced in which 90% by volume was composed of the gold-rich liquid phase. This alloy contained 23.4 atomic percent rhodium. During the later stages of the investigation, a third alloy composition was produced which contained 80% by volume of the gold-rich liquid phase (29.2 atomic percent rhodium).

The samples investigated were produced by melting and alloying the pure components in a small, copper hearth arc furnace. A tungsten electrode was utilized and melting was done under an argon atmosphere. Sample masses ranged from approximately 150 to 500mg.

In this investigation, samples were levitated and melted at the top of the drop tube using an electromagnetic levitation furnace. Each sample was heated to as high a temperature as possible and then released. Solidification took place during free fall, which provided low gravity containerless processing conditions. Absolute sample temperatures could not be accurately determined due to difficulties encountered with the non-contact temperature measurement technique

utilized. Calibrated non-contact temperature measurements are planned for future studies. It should also be pointed out that there is disagreement in the literature as to the exact shape and temperature of the miscibility gap in the Au-Rh system. This makes it difficult to determine if the single phase region was reached during heating.

There are several limitations to the use of a drop tube. One of the most severe is that the free fall time is quite limited; 4.6 seconds for a 105 meter tube. As a result, it is necessary to use small samples and to process alloys that possess fairly high melting points so that high rates of heat loss from radiative cooling are achieved. In the case of alloys with long freezing ranges, as in most immiscible alloys, it may be necessary to increase the cooling rate in the tube by partially back filling with an inert gas which provides additional cooling due to convection. This compromises the quality of the low gravity conditions somewhat. However, this approach was utilized in the current study with no deleterious effects. Calculated g-levels in the 10^{-2} g range would have been expected during solidification of the samples processed in this study (Ref. 9).

One system dependent difficulty encountered with the processing of gold-rhodium alloys was a tendency for the samples to fall from the levitation coil due to a lack of levitating force at elevated temperatures. In many cases it was not possible to hold the sample at the required temperature for the time desired. Several different approaches were utilized to help alleviate this difficulty with the most successful being the custom design of a specialized high lifting force levitation coil for the gold-rhodium samples.

3. RESULTS AND DISCUSSION

The sample shown in Figure 4 is typical of one containing 10 percent by volume of the gold-rich hypermonotectic phase (65 atomic percent rhodium alloy composition) after alloying in the arc melter. This sample solidified under one-g conditions and as a result experienced sedimentation of the more dense, gold-rich liquid. The rhodium rich region in the upper portion of the sample is of approximately monotectic composition. The lower, gold-rich region is the same composition as L_2 at the monotectic temperature.

Obviously, low gravity, containerless processing was expected to give different results. For this 10% gold-rich hypermonotectic phase composition, two distinctly different types of microstructure were obtained. Approximately one half of the samples exhibited structures with an interconnected gold-rich phase. These samples often had a gold-colored outer surface. A section through one of these 10% gold-rich liquid samples is shown in Figure 5. In the majority of samples of this type, the entire structure consisted of a high volume fraction of the rhodium-rich phase containing an interconnected gold-rich phase. A section through a different 10% gold-rich phase sample is shown in Figure 6. This sample formed a dispersion of the gold-rich phase in a rhodium-rich matrix as opposed to an interconnected structure. While several of these samples had a relatively fine and uniform dispersion of the gold-rich phase, most contained a few rather large (0.5-1.0mm diameter) spherical regions of the gold-rich phase (Figure 7). Most of the samples of this composition had a coating of the gold-rich phase along the outer surface.

To recap, alloys containing 10% by volume of the gold-rich hypermonotectic liquid had two distinctly different microstructures. One in which the gold-rich phase was interconnected and another which was often dispersed and not continuous. The processing procedures that produced these two structures were very similar.

As discussed above, many of the 10% by volume gold-rich phase samples (65 atomic percent rhodium) exhibited a tendency for the minority immiscible liquid to wet the outer surface. This resulted in macroscopic separation of the immiscible phases in about one-half of the samples. If separation is caused when the minority phase wets the outer surface of the droplet, it should be much easier to form a dispersion if the relative proportions of the two phases were switched. In order to further study the ability to form dispersed structures in this system, an alloy composition was investigated which contained a volume fraction of 90% (as opposed to 10%) of the gold-rich phase.

Figure 8 shows a photomicrograph of a 90% gold-rich hypermonotectic phase sample (23.4 atomic percent rhodium) that was processed under low gravity containerless conditions using the drop tube. This sample contained a dispersion of rhodium-rich spheres which ranged in size from 20 to 5 μ m in diameter. It is apparent from the phase diagram that when this particular alloy composition cools, separation into L_1

and L_2 is expected above the monotectic temperature (90% L_2 is expected). The L_1 liquid, which would most likely be present as spherical droplets dispersed in the L_2 phase, would then go through monotectic decomposition on cooling to form the rhodium-rich solid and additional L_2 . Since the monotectic composition is closest to the rhodium end of the tie line, the rhodium will serve as the matrix phase for the monotectic constituent formed from the L_1 . Therefore, spherical regions consisting of the rhodium-rich monotectic structure, dispersed in a gold-rich liquid are expected at temperatures just below the monotectic. As the sample cools toward the lower temperature gold-rhodium peritectic, the solubility of rhodium in the gold-rich liquid phase decreases and precipitation (or solidification) of almost pure rhodium is expected. Close examination of several samples at high magnification revealed the presence of small rhodium dendrites.

In several locations on this sample it appeared as if the rhodium-rich spheres had come in contact with one another but had not coalesced. These particles were most likely solid when they touched. As can be seen from the phase diagram, there is a rather extensive temperature region over which the primarily solid, monotectic composition, rhodium-rich particles would be present in the molten, gold-rich liquid phase.

The above sample (Figure 8) definitely exhibited a dispersion of one of the immiscible phases in the other and should be contrasted with the interconnected structure (Figure 5) obtained in many of the 10 percent gold-rich phase samples. Indeed, out of eight 90% gold-rich liquid samples analyzed after low-gravity containerless processing, every sample possessed a dispersed microstructure. These dispersions ranged from relatively coarse, approximately 0.4 mm diameter, to relatively fine 2-3 μ m diameter, rhodium-rich spheres in a gold-rich matrix. An example of one of the best dispersions obtained is shown in Figure 9 for a 90% gold-rich liquid sample. This sample contained roughly spherical rhodium-rich particles having a 2 to 3 micrometer diameter which were uniformly distributed throughout. Most samples exhibited dispersions with mean particle diameters ranging from 3 μ m up through approximately 10 μ m.

A few samples of the 90% gold-rich composition exhibited microstructures which were much more coarse than those discussed above. While the structures were still basically a dispersion of rhodium-rich spheres in a matrix of the gold-rich phase, some of these rhodium-rich spheres (Figure 10) had diameters approaching 1.0mm. It has been speculated that this structure resulted because the samples were not heated to a sufficiently high temperature. If they had not reached the single liquid region but were above the monotectic temperature, the two immiscible liquid phases would have been present while the sample was held in the levitation coil. This would have provided an extended time period for coalescence, and could have led to the formation of large rhodium-rich spheres. Unfortunately, reliable temperature data is not available for these samples. However, results obtained for other samples of this composition which exhibited well dispersed structures, indicate the temperatures may

have been marginal in several cases. Further experimentation is necessary to quantify the effect of experimental conditions on the final sample microstructure.

It was apparent that the volume fraction of the rhodium-rich phase in these 90% gold-rich phase samples was higher than that anticipated from the phase diagram. As previously pointed out, there is disagreement among investigators on the compositions of the phases at the monotectic temperature. This could account for the different volume fraction than anticipated. Another possibility lies in alloy composition changes that result due to volatilization of the lower melting gold-rich liquid during processing. Some volatilization was evident when processing samples of this composition.

While the structures obtained in the 90% gold-rich phase alloys were very desirable, there was still some question as to how the structure of the immiscible alloys would vary with the relative volume fraction of the two phases. In order to gain more information in this area, several samples were prepared which contained 80% by volume of the gold-rich phase, as determined from the phase diagram.

A photomicrograph of an 80% gold-rich hypermonotectic phase sample (29.2 atomic percent rhodium) processed under low-g containerless conditions is shown in Figure 11. This sample possessed a structure very similar to those obtained in the majority of the 90% gold-rich phase samples. The structure was dispersed and contained rhodium-rich spheres ranging in diameter from 2 to 50 micrometers. The structures of most 80% gold-rich liquid phase samples were similar to this sample. However, again for this composition, several samples were produced that contained large spherical regions of the rhodium-rich phase. These regions approached 0.7mm in diameter.

Several of the finely dispersed 80% gold-rich liquid samples appeared to contain a very high percentage of the rhodium-rich phase. Many of these small spherical regions touched in several locations and appeared to be approaching the "packing limit". Obviously, if the volume fraction of the rhodium-rich phase is continuously increased above that which was utilized in this sample, the structure would change. Eventually the situation would be reached where spheres of the rhodium-rich phase in a gold-rich matrix would be replaced by a structure consisting of spheres of the gold-rich phase in a rhodium-rich matrix. It is reasonable to assume that a transition structure would be encountered as the volume fraction of the two phases shifts, where the gold-rich phase would be continuous and interconnected in the rhodium-rich phase. In future work, a systematic variation in the volume fraction of the two phases will be carried out to study these changes in morphology.

4. GENERAL OBSERVATIONS

To summarize, even though accurate temperature data is not available at this time and our findings must be considered preliminary the following observations can be made from this investigation:

1. There is a tendency for the gold-rich immiscible liquid phase to wet the outer surface of immiscible gold-rhodium alloys processed under low-g, containerless conditions.
2. In alloys where the rhodium-rich immiscible phase is the majority phase, the gold-rich phase is often interconnected throughout the alloy.
3. Dispersed microstructures are more easily obtained when the gold-rich immiscible phase is the majority phase and serves as the matrix.
4. In the best samples, fine dispersions consisting of 2 to 3 micrometer diameter rhodium-rich spheres in a gold-rich matrix have been obtained through solidification of small samples under containerless low gravity conditions.

5. ACKNOWLEDGEMENTS

The authors would like to acknowledge Ms. Sharon Cobb, Ms. Nancy Toliver, and Mr. Jeff Conner for their assistance in sample preparation and analysis during the early stages of this study. Thanks also go to Mr Tom Rathz for his assistance with the drop tube.

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Table 1. Alloy Compositions Investigated

Amount of Gold-Rich Hypermonotectic Phase	Alloy Composition (atomic %)
10%	65.0% Rh
80%	29.2% Rh
90%	23.4% Rh

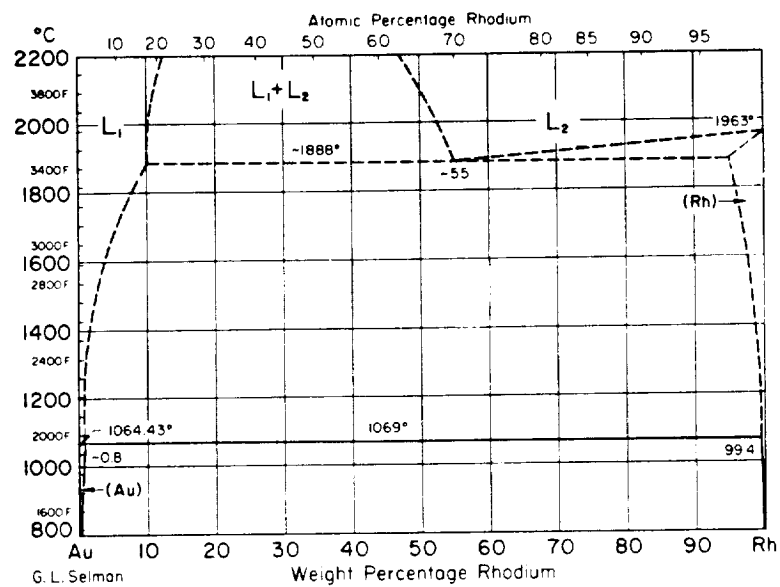


Figure 1. The Gold-Rhodium phase diagram. (From Ref.2)

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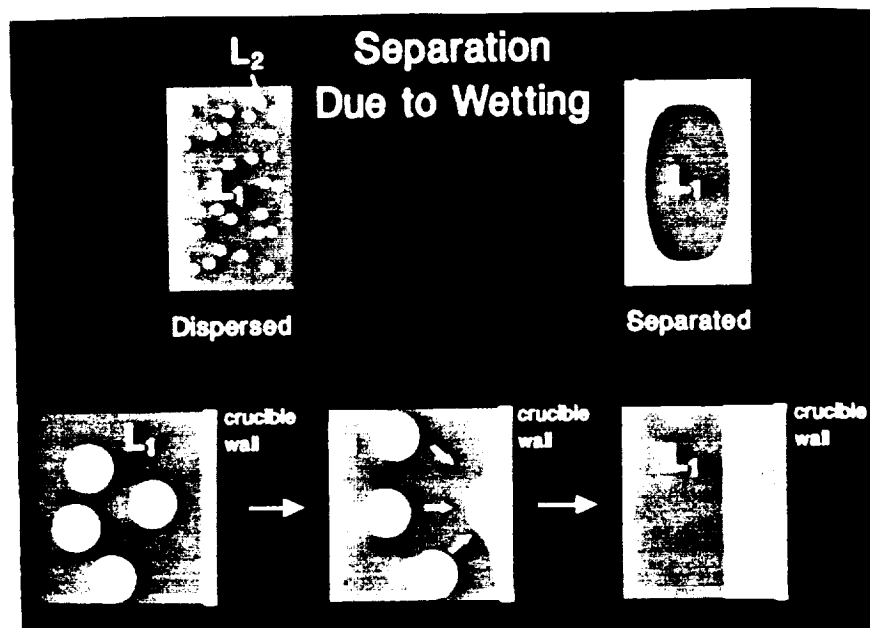
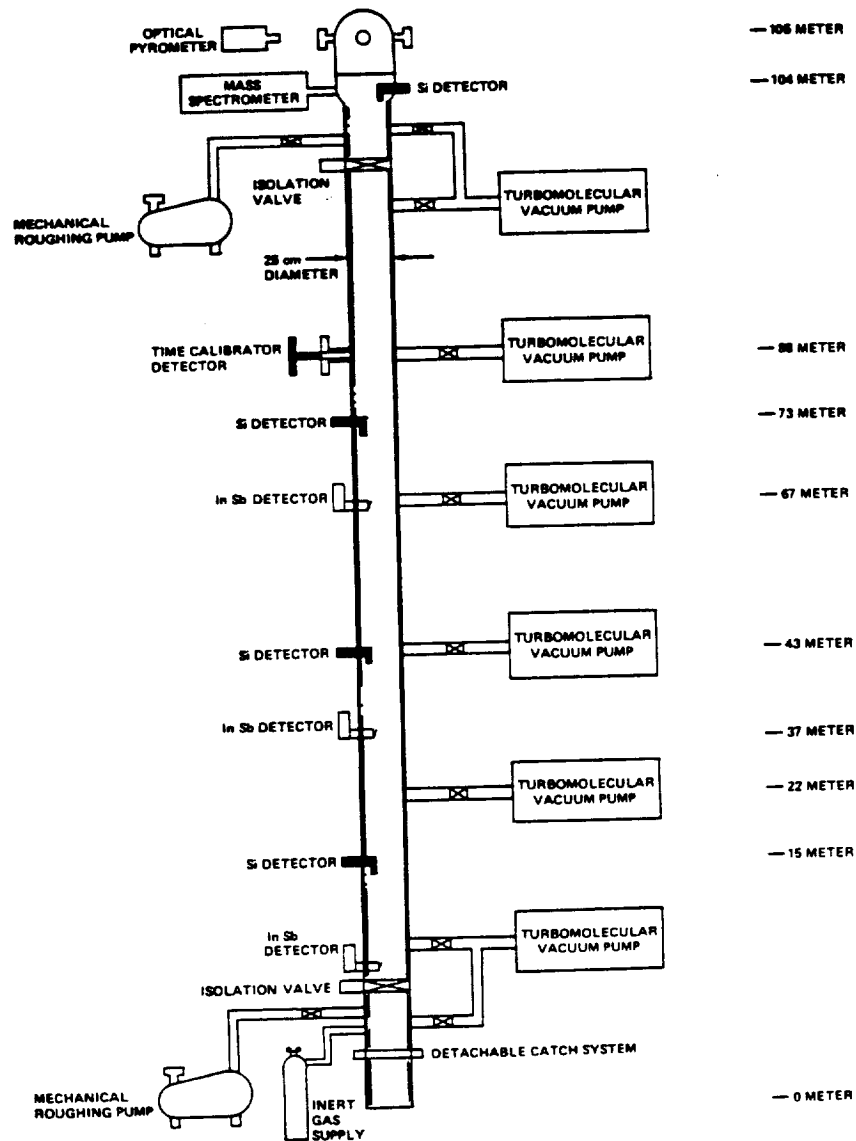


Figure 2. Schematic representation of one possible sequence of events that leads to separation of L_1 and L_2 . During cooling, dispersed L_2 droplets form in L_1 . If L_2 touches and perfectly wets the container wall, the fluid flow that results may pull additional L_2 to the wall. This L_2 could, in turn, perfectly wet the wall causing a repeat of the above sequence of events. The final result would be complete separation of L_1 and L_2 .



MARSHALL SPACE FLIGHT CENTER 105 METER DROP TUBE FACILITY

Figure 3. Schematic diagram of the Marshall Space Flight Center 105 meter drop tube. (From reference 9.)

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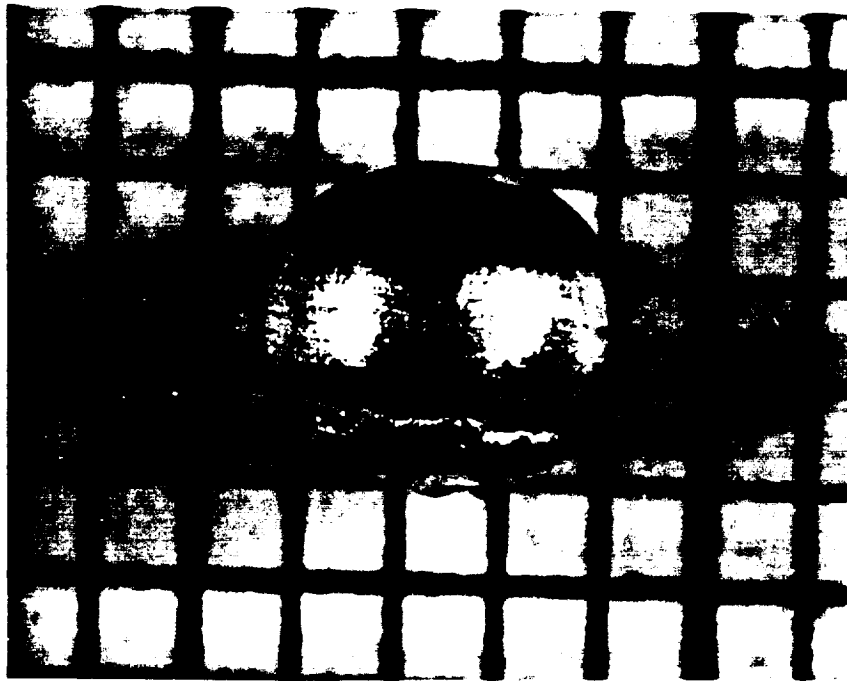


Figure 4. A typical sample containing 10 percent by volume of the gold-rich hypermonotectic phase (65 atomic percent rhodium) after alloying in an arc melter under one-g conditions. Note sedimentation. Each scale division = 1 mm.

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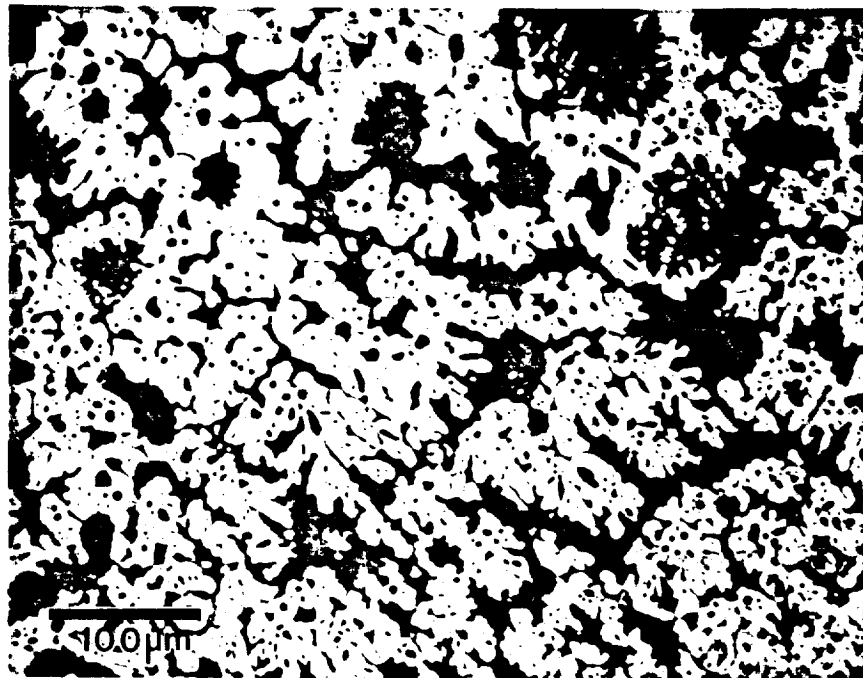


Figure 5. A drop tube processed sample containing 10 percent by volume of the gold-rich hypermonotectic phase (65 atomic percent rhodium). The gold-rich phase appears to be interconnected.

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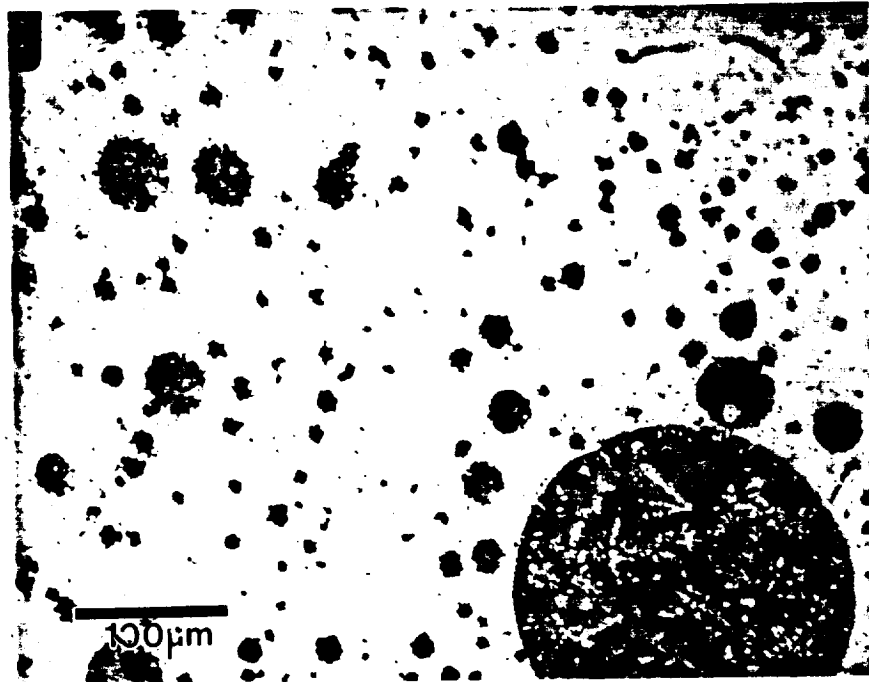


Figure 6. A different 10 percent gold-rich phase sample (65 atomic percent rhodium) produced in the 105 meter drop tube. In this sample, the gold-rich phase appears to be dispersed instead of interconnected as was shown in Figure 5.

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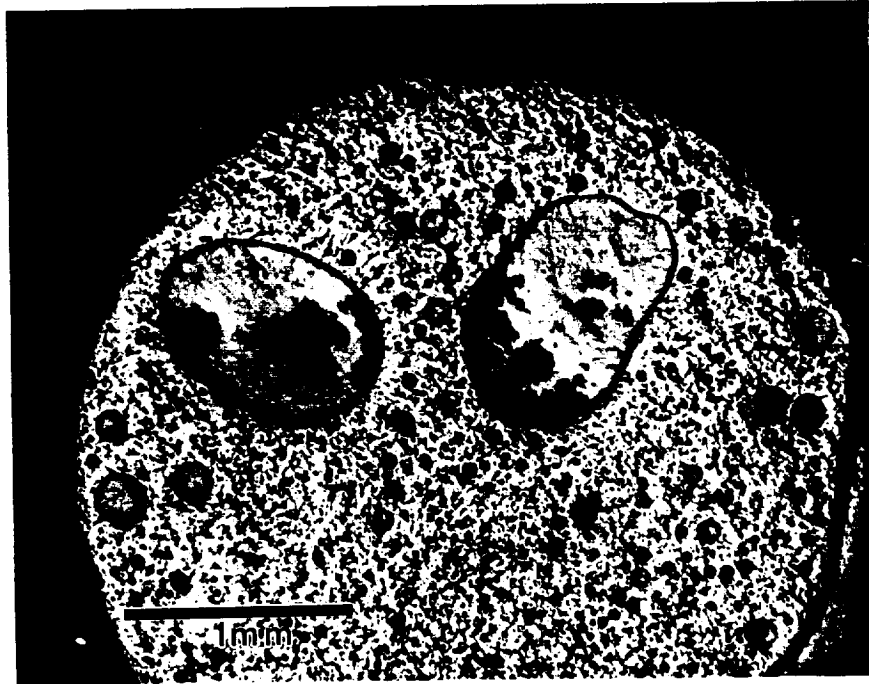


Figure 7. Cross-section of a 10 percent gold-rich phase sample processed under low-g containerless conditions which produced a disconnected structure and exhibited several large diameter (0.5mm) spherical gold-rich regions.

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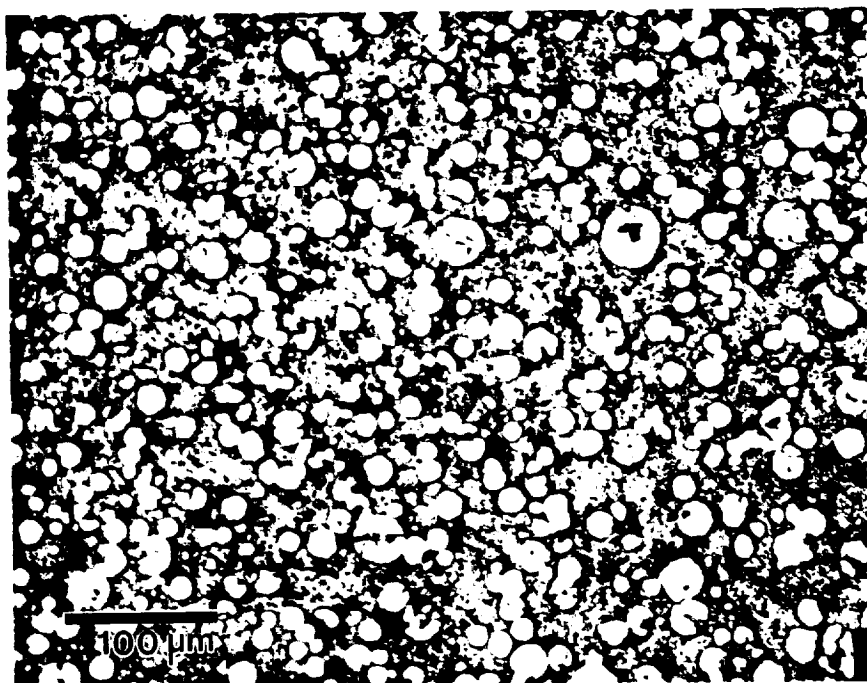


Figure 8. Cross-section of a 90 percent gold-rich phase sample that was low-g processed showing a dispersion of rhodium-rich spheres in a gold-rich matrix.

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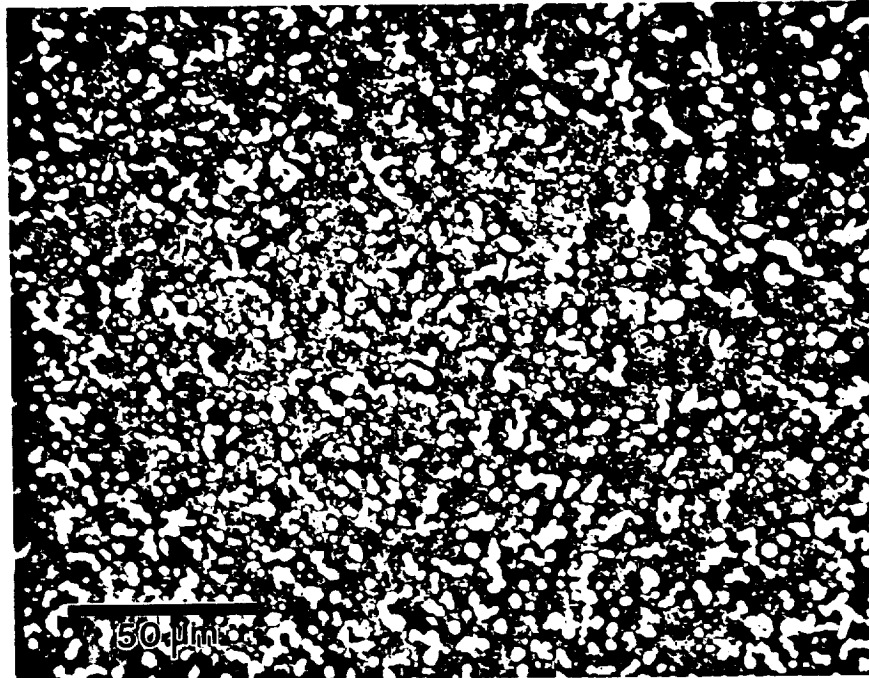


Figure 9. A finely dispersed microstructure obtained in a 90 percent gold-rich phase (23.4 atomic percent rhodium) sample processed under low-g containerless conditions. The diameter of the rhodium-rich particles range from 2 to 3 micrometers.

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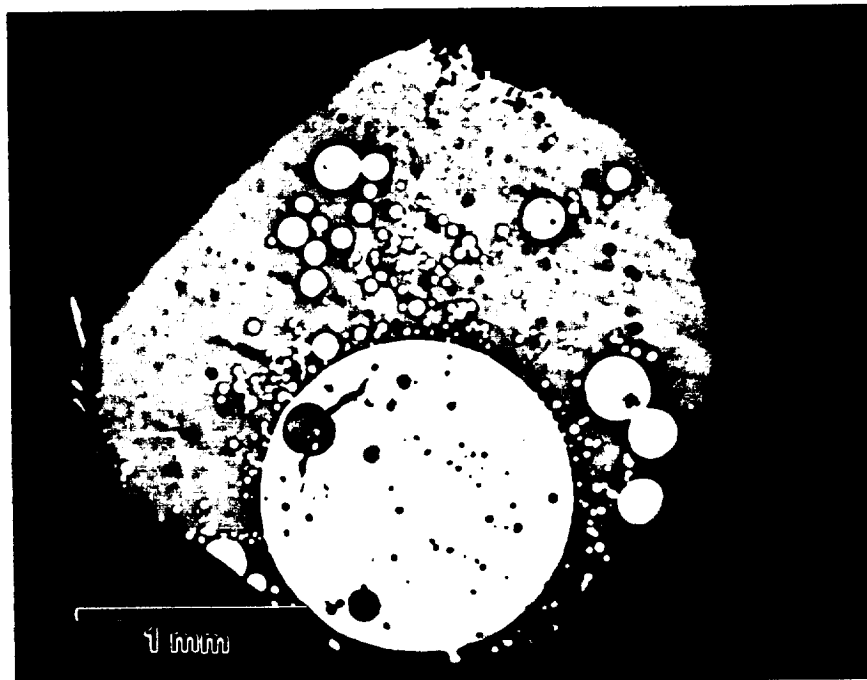


Figure 10. Microstructure of a 90% gold-rich phase sample which contained large spherical regions of the rhodium-rich phase.

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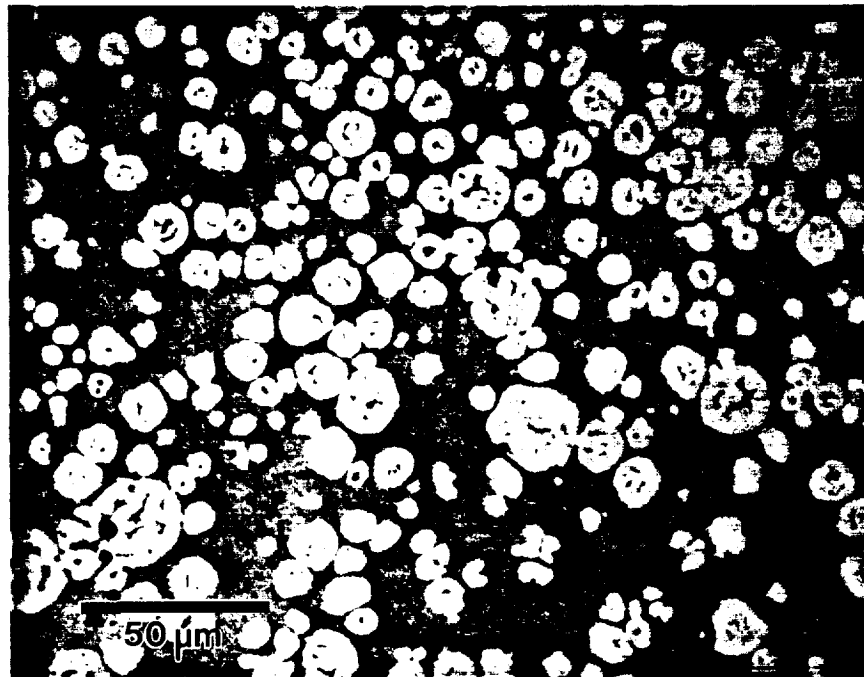


Figure 11. Microstructure of an 80% gold-rich phase sample processed under low-g containerless conditions.